# CALIBRATION OF ZIRCONIUM-OXIDE OXYGEN SENSOR FOR MEASURING OXYGEN CONCENTRATION IN LIQUID LEAD-BISMUTH EUTECTIC

Alan Michael Bolind
Graduate Research Assistant, Advanced Accelerator Applications-TPO
Los Alamos National Laboratory
MS H816, 53-18-124
P.O. Box 1663, Los Alamos, NM 87545
Telephone: (505) 665-5623  Fax: (505) 667-7443  Email: abolind@lanl.gov

## ABSTRACT

Work is being done at Los Alamos National Laboratory to develop liquid lead-bismuth (Pb-Bi) eutectic (LBE) for use as a coolant fluid, and perhaps also as a spallation target, in new nuclear energy systems. However, LBE presents a long-term corrosion problem with some materials, notably stainless steels, which are often used for nuclear piping systems. It is possible to prevent most corrosion by monitoring the dissolved oxygen level in the LBE and controlling it to be within high and low limits. Monitoring can be accomplished using yttrium-stabilized zirconium-oxide oxygen sensors, which produce voltages corresponding to oxygen differentials between a reference and the oxygen in the LBE. Although theory can predict the order of magnitude of these voltages, calibration is necessary to determine actual performance.

## INTRODUCTION

Work is being done at Los Alamos National Laboratory to develop liquid lead-bismuth (Pb-Bi) eutectic (LBE) for use as a coolant fluid, and perhaps also as a spallation target, in new nuclear energy systems. However, LBE presents a long-term corrosion problem with some materials, notably stainless steels, which are often used for nuclear piping systems. There are two main forms of corrosion: (1) oxidation of the iron in the steel (better known as rust), and (2) "leaching out" the nickel from the stainless steel alloy. In this second form of corrosion, the LBE actually dissolves the nickel from the steel, which causes the material to become embrittled and prone to failure. These corrosion phenomena need to be controlled if LBE is ever going to be used for long-term systems.

Fortunately, these two forms of corrosion are both related to the amount of oxygen that is dissolved in the liquid LBE. Iron oxidation becomes a problem when there is too much oxygen in the LBE, whereas nickel leaching occurs when there is too little oxygen. As Li has pointed out [1], the theory is that just enough oxygen in the LBE will cause a very thin oxide layer to form on the surface of the material (for example, on the inside of a pipe), which will shield the material from nickel leaching; but too much oxygen will cause too much rust. Therefore, it is possible to prevent both forms of corrosion by monitoring the dissolved oxygen level in the LBE and controlling it to be within these high and low limits.

The instrument used to monitor the dissolved oxygen level ⊟ solid-electrolyte sensor. The sensor element is a ceramic cone, made of yttrium-oxide-stabilized zirconium oxide (YSZ).

Although at low temperatures, YSZ acts as an electrically insulating material, it does become conductive to oxygen ions ($O^{2-}$) when it reaches high temperatures, around 350°C. When the concentration of oxygen on one side of the YSZ ceramic electrolyte is different from the concentration on the other side, oxygen ions migrate through the electrolyte from the side of high concentration to the side of low concentration. As they migrate, they bring negative charge to the side of low concentration, thus causing a voltage to develop across the electrolyte. This voltage can be measured with a high-impedance electrometer. Since the voltage is dependent on the difference in oxygen concentrations on the two sides of the electrolyte, it can be directly correlated through experiment. Therefore, by knowing beforehand the concentration on one side (called the reference electrode) and by using the voltage to determine the difference in oxygen concentrations, one can calculate the unknown oxygen concentration on the other side. A schematic picture of this technique is shown in Figure 1.

The theory that governs this voltage phenomenon is the Nernst equation, which yields the theoretical voltage potential across an electrolyte for a given set of ambient conditions and a difference of oxygen concentration between the two sides of the electrolyte. One form of the Nernst equation is as follows [2]:

$$V_m = \frac{RT}{4F} \ln \frac{P_{O_2}}{P_{O_2}(\text{Ref})}$$  (1)

where $V_m$ = the expected voltage, in volts

$R$ = the universal gas constant, which is $8.314510 \ \dfrac{\text{Pascals-m}^3}{\text{Kelvins-moles}}$, [3]

$T$ = the temperature of the system, in Kelvins
$F$ = the Faraday constant, which is 96485.3415 Coulombs/mole [3]
$P_{O_2}$ = the partial pressure of oxygen dissolved in the liquid LBE, in Pascals
$P_{O_2}(\text{Ref})$ = the partial pressure of oxygen in the reference material, in Pascals
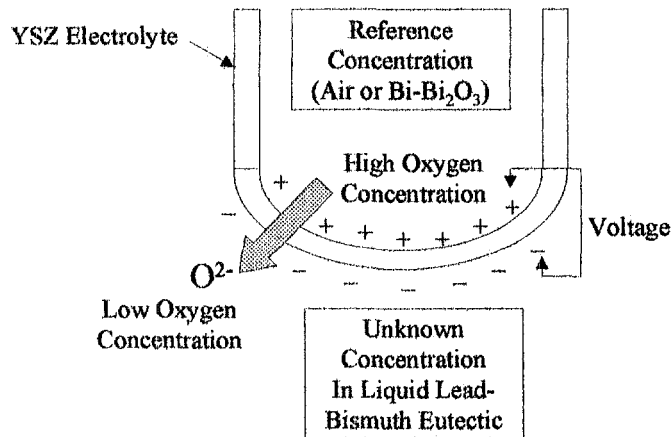
## Schematic of YSZ Sensor Operation



Figure 1: Schematic picture of oxygen sensing using a YSZ ceramic electrolyte

When dealing with dilute liquid solutions rather than gases, the partial pressures can be replaced by concentrations, expressed as molalities in units of moles of solute per kilogram of solvent [4].

Also note that the magnitude of the voltage is what is important; the sign of the actual voltage observed will depend on the manner in which the electrometer is connected to the sensor.

A reasonable value for the temperature is 673 K (400°C). For a reference concentration, many options are available; air or an equilibrium mixture of bismuth and bismuth oxide ($Bi/Bi_2O_3$) are of particular interest for this project. The partial pressure of oxygen in the atmosphere varies, but a typical value is about 0.21 atmospheres, or 21 kPa [3]. The concentration/partial pressure of oxygen in $Bi/Bi_2O_3$ can be calculated from the following formula [1], based upon the free energy of formation of $Bi_2O_3$:

$$P_{O_2} = e^{9.82 - \frac{20275}{T}} \qquad (2)$$

where $P_{O_2}$ = the partial pressure of $O_2$ dissolved in the liquid Bi/solid $Bi_2O_3$, in atmospheres

T = temperature, in Kelvins

Thus, at 400°C, the partial pressure of oxygen in $Bi/Bi_2O_3$ is $1.52 \times 10^{-9}$ atmospheres, or $1.54 \times 10^{-4}$ Pascals.

Unfortunately, actual results usually do not follow the theoretical predictions of the Nernst equation. Many other phenomena, such as slight electrical conductivity of the YSZ and thermocouples between metals, can influence the voltage produced. Therefore, the sensors must be calibrated against known concentrations of oxygen in LBE and/or gas. This calibration is the goal of current efforts.

METHODS

Two types of calibration are currently being undertaken: calibration in gases, and calibration in liquid LBE. The reason both types are being performed is that the test piping system (or, "loop") that is being constructed at Los Alamos National Laboratory will use sensors in both situations: (1) to measure directly the oxygen content in the liquid LBE, and (2) to measure the oxygen content of the cover gases that exist above the LBE surface in certain tanks in the loop. Therefore, two different types of sensors and calibration apparatus are being used.

The test setup for gas calibration consists of a pipe tee, with a sensor mounted in the bull of the tee, a connection for gas on one end of the run of the tee, and a flange with a hole for a thermocouple on the other end of the run of the tee. The sensor is a Bosch® Oxygen Sensor, model 13913, which uses air as a reference and is used in automobiles to measure the oxygen content of the engine exhaust. A Keithley high-impedance electrometer (model 614) measures the voltage produced by the sensor. A DC source provides 12VDC to the internal heater in the sensor. A tape heater wrapped around the pipe provides external heating and is electronically controlled to maintain the gas temperature inside the tee at a pre-determined set point. Another thermocouple measures the temperature of the flange where the sensor is located. Bottled gases can be pumped into the tee, using the gas connection. Also, the gas connection can be removed to allow plain air into the pipe. The use of these gases provides three calibration points—zero oxygen ($N_2$), 6% oxygen (6%-$O_2$/bal-He), and 21% oxygen (air)—referenced to air.

The test setup for calibration in liquid LBE consists of a length of pipe with elbows on either end. Molten LBE that has been skimmed of contaminants is poured into the pipe. An

oxygen sensor has been welded into the middle of the pipe. This sensor was designed at the laboratory and uses a YSZ element similar to the one in the Bosch sensor. Flange connections attached to the two elbows enable the pipe to be sealed off or provide gas connections. A tape heater, wrapped around the pipe and electronically controlled via a thermocouple in the pipe, maintains the temperature of the LBE at a pre-determined level.

The calibration of the liquid sensor can be done at a minimum of two points for each type of reference (air or $Bi/Bi_2O_3$) used: (1) oxygen-saturated LBE, and (2) oxygen-free LBE. Oxygen-saturated LBE can be obtained either by leaving the sealing flanges off the elbows and exposing the LBE inside the pipe to air or by blowing 6%-$O_2$/bal-He through it. Either method will cause more and more oxygen to dissolve into the LBE until lead oxide (PbO) begins to form, at which point the LBE is saturated with oxygen. The oxygen content of saturated PbO is given by the following formula, similar to the formula used for $Bi/Bi_2O_3$ [1]:

$$P_{O_2} = e^{10.55 - \frac{23060}{T}} \tag{3}$$

Oxygen-free LBE can be obtained by blowing a mixture of 6%-hydrogen/balance-helium through the LBE. The hydrogen reacts with the oxygen in the LBE to form steam. From experiment, about 18 hours are needed to deoxygenate oxygen-saturated LBE.

RESULTS AND DISCUSSION

Calibration of the Bosch® oxygen sensor is gas is still underway. Several difficulties have been encountered, which have helped to define the operating parameters of the sensor. The first tests were conducted using only the sensor's internal heater and not the tape heater also. Low, unstable, and unrepeatable voltages were observed. It is known that the sensor electrolyte was hot enough to conduct oxygen ions, because (1) a heater element from a sensor was measured to reach over 500°C and (2) the voltage readings were not sensitive to external influences (such as touching the electrometer leads), indicating that ionic conduction was occurring to override such influences. It is believed that the cause of these poor results was due to the room-temperature gas conducting heat away from the sensor faster than the sensor's heater could heat its surroundings. These observations indicate that it probably not possible to measure the oxygen content of a gas at room temperature; instead, both the gas and the sensor itself must be hot. The fact that the second set of tests with the tape heater operating produced somewhat better results lends evidence to this hypothesis.

In the second set of gas calibration tests, the tape heater was on. Results of one such test are presented in Figure 2. In this test, almost pure nitrogen gas (i.e., almost no oxygen) was put into the test pipe. The sensor's internal heater was not turned on until the internal gas temperature had reached about 300°C. Figure 2 shows that at that point, the sensor became active and began to read reasonable values (around 0.8 volts). However, the voltage dropped over time, plummeting to about 0.15 volts within 45 minutes. This phenomenon occurred repeatably and with two different Bosch® oxygen sensors. The cause for this phenomenon is not yet clear. One hypothesis is that the oxygen on the reference side of the electrolyte is being depleted by oxidation of the plastic or metal parts of the sensor. More experimentation is necessary to determine the cause of the instability and develop a solution.

Tests on gases other than nitrogen were also performed. However, unreliable readings were obtained. The voltage obtained with air in the pipe and with both heaters on was approximately –0.03 (sign is relative to the nitrogen reading).
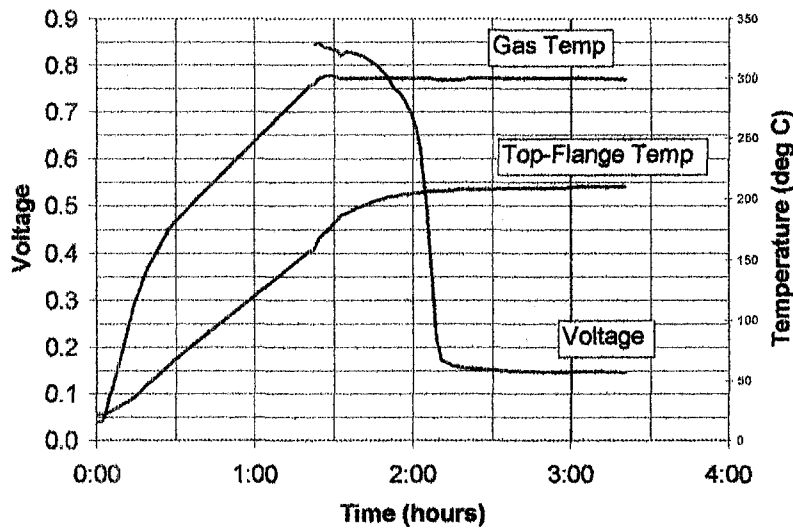


Figure 2: Performance of Oxygen Sensor in "Pure" Nitrogen Gas

The majority of the test apparatus for calibrating the sensor in liquid LBE has been constructed. However, the apparatus had yet to be completely assembled, and, therefore, tests have not yet been conducted.

CONCLUSION

Oxygen sensing with YSZ sensors is theoretically possible and has been experimentally verified. However, calibration must still be performed to relate observed voltage to actual oxygen concentration. This calibration is still underway at the laboratory.

REFERENCES

1.   Li, Ning. "Active Control of Oxygen in Molten Lead-Bismuth Eutectic Systems to Prevent Steel Corrosion and Coolant Contamination." LANL Paper, LA-UR-99-4696.
2.   Madou, Marc J., and Morrison, S. Roy. *Chemical Sensing with Solid State Devices.* Boston: Academic Press. 1989.
3.   Lide, David R., ed. *CRC Handbook of Chemistry and Physics.* 81st ed. Boca Raton: CRC Press. 2000.
4.   Hampel, Clifford A., ed. *The Encyclopedia of Electrochemistry.* New York: Reinhold Publishing Corporation. 1964. Entry on "Nernst Equation."

# Calibration Of Zirconium-Oxide Oxygen Sensor For Measuring Oxygen Concentration In Liquid Lead-Bismuth Eutectic

Alan Bolind

Los Alamos National Laboratory

Symposium 2001

August 6, 2001

1

# Outline of Presentation

- Background – Lead-Bismuth Eutectic and Oxygen Sensing
- Theory – the Nernst Equation
- Calibration Apparatus
  - ◆ In Gas
  - ◆ In Liquid Lead-Bismuth
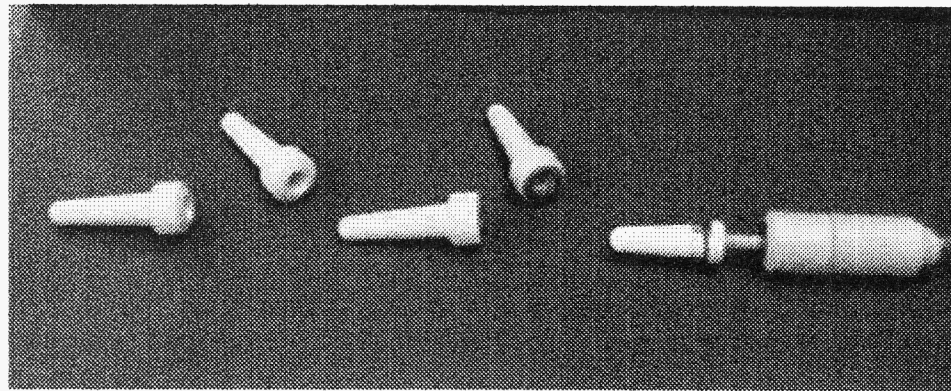- Results
- Conclusion

# Background

- Lead-Bismuth Eutectic (LBE) is good for:
  - ◆ Cooling
  - ◆ Spallation Target
- LBE corrodes stainless steel pipe:
  - ◆ Dissolves nickel
  - ◆ Clogs with rust
- Solution: Control dissolved oxygen in LBE to prevent corrosion

# Material Test Loop





4
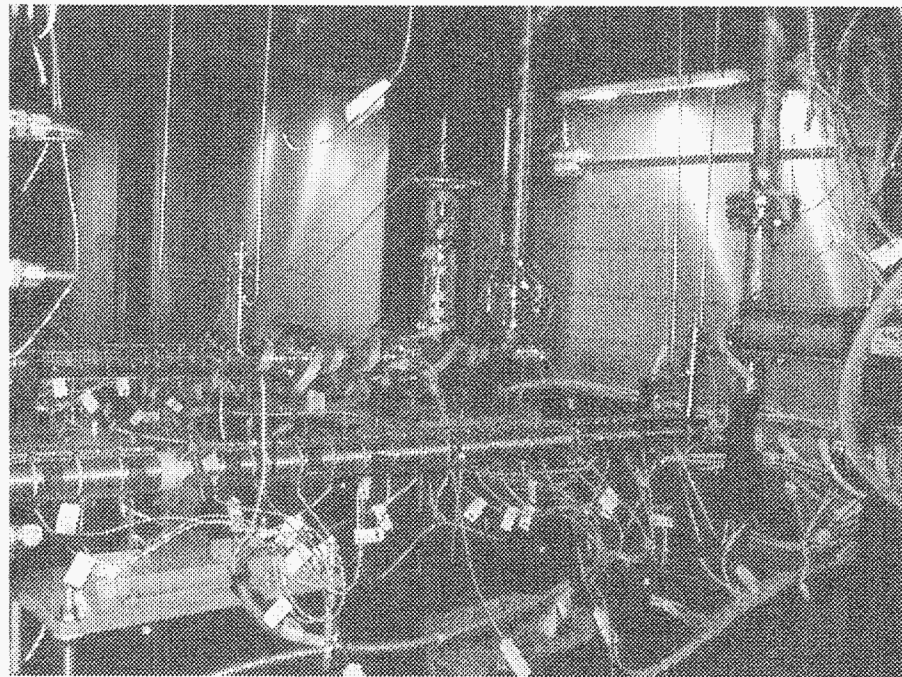
# Oxygen Sensors

- Sensors are ceramic YSZ
- Used in automobiles
- Work above 350°C

# Schematic of YSZ Sensor Operation



YSZ Electrolyte

Reference
Concentration
(Air or Bi-Bi$_2$O$_3$)

High Oxygen
Concentration

Voltage

$O^{2-}$

Low Oxygen
Concentration

Unknown
Concentration
In Liquid LBE
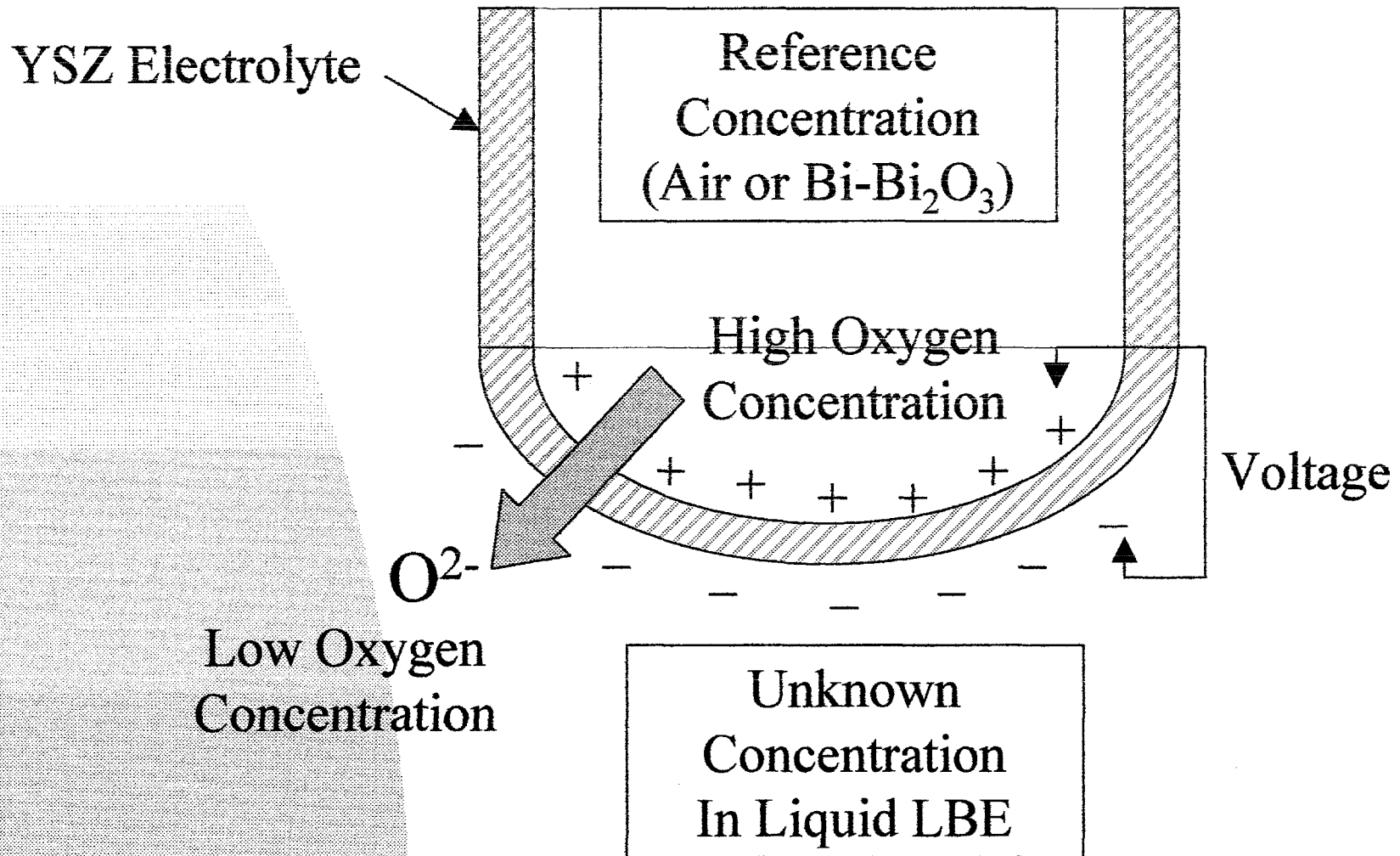
# Theory—Nernst Equation

$$V_m = \frac{RT}{4F} \ln \frac{P_{O_2}}{P_{O_2}(\text{Ref})}$$

- Known:
  - ◆ Voltage
  - ◆ Oxygen in Reference
- Find:
  - ◆ Oxygen in Gas or LBE

# Apparatus for Calibration in Gas
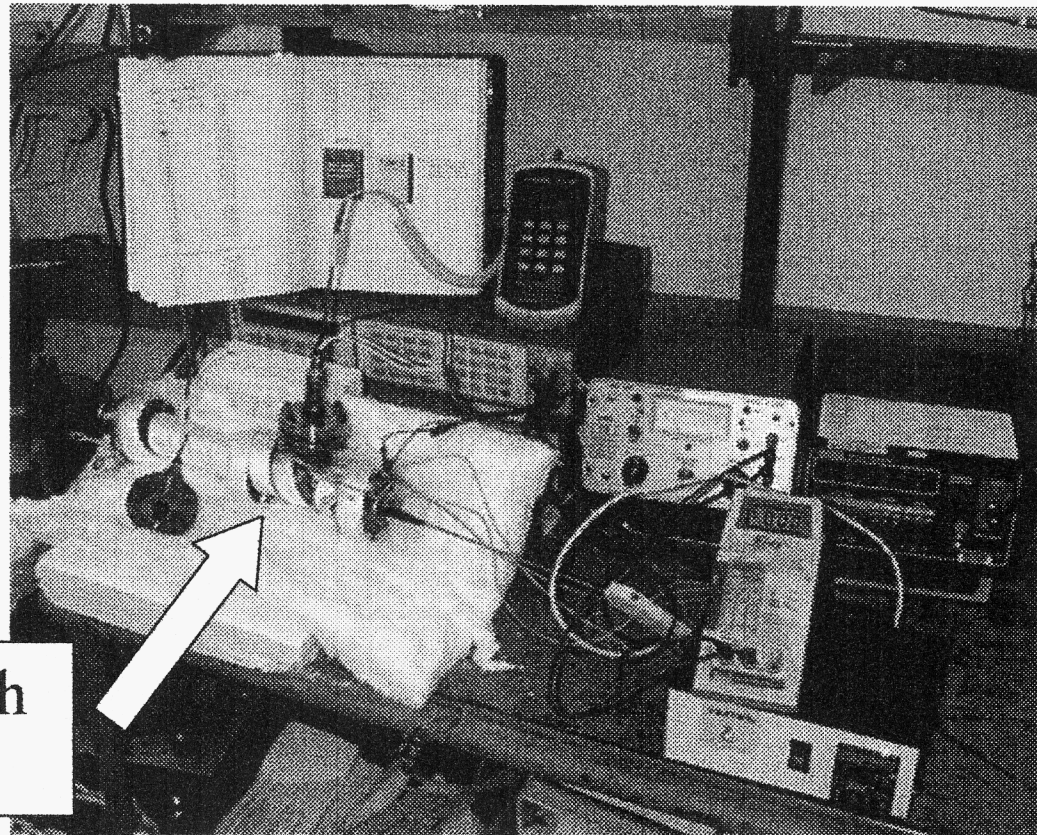


Pipe Tee with Sensor

# Gas Results—Unstable
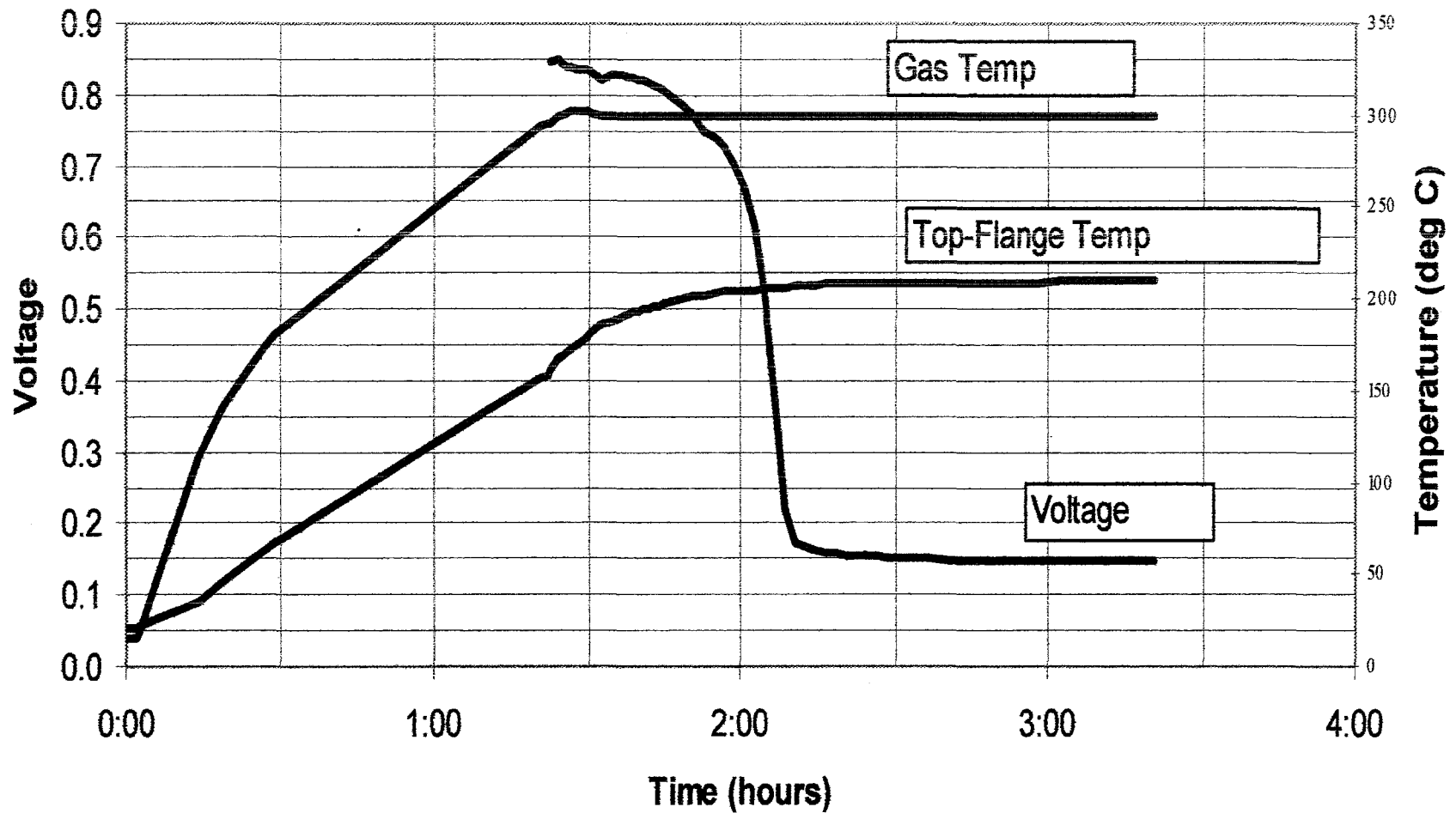
# Apparatus for Calibration in LBE



Oxygen Sensor
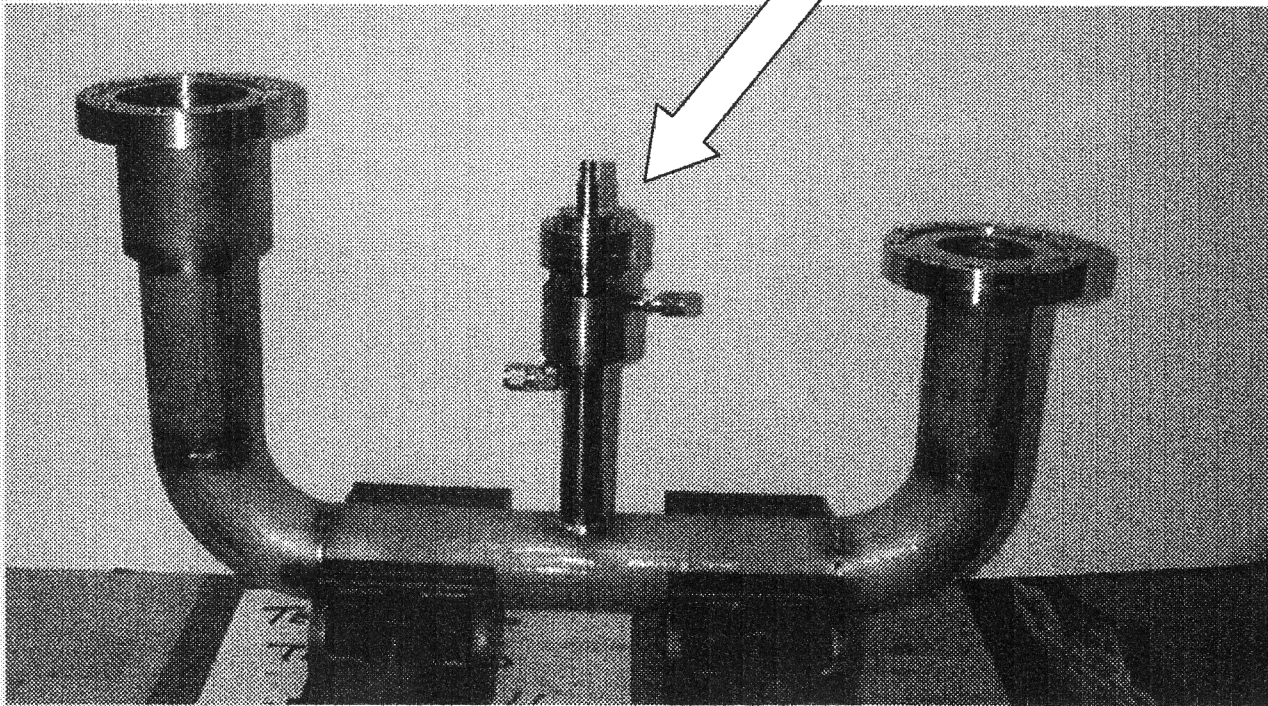
# Conclusion

- Calibration in gas is possible, but we need to make it more stable
- Calibration in liquid LBE is next

GAS
$O_2$ SENSOR
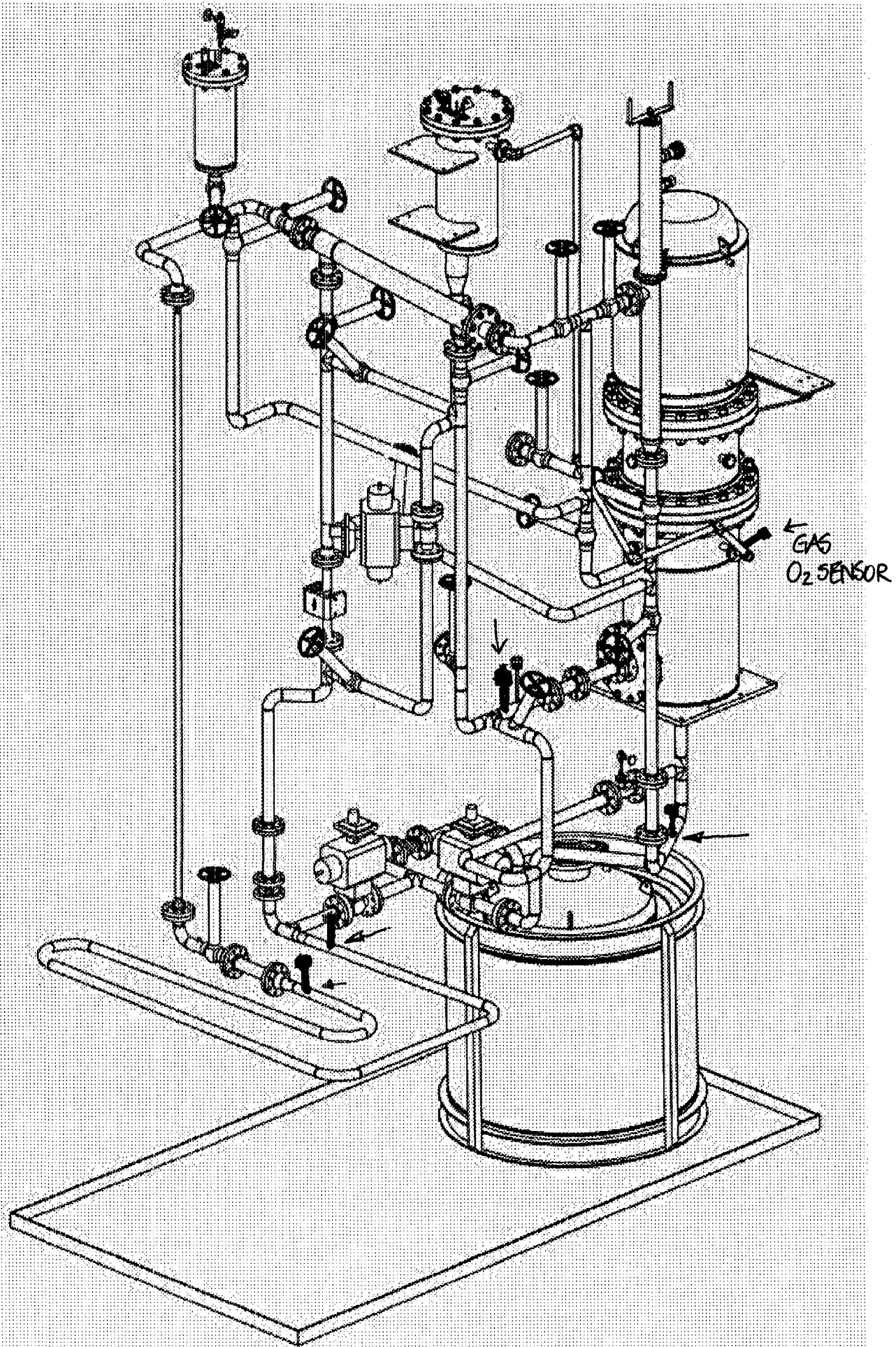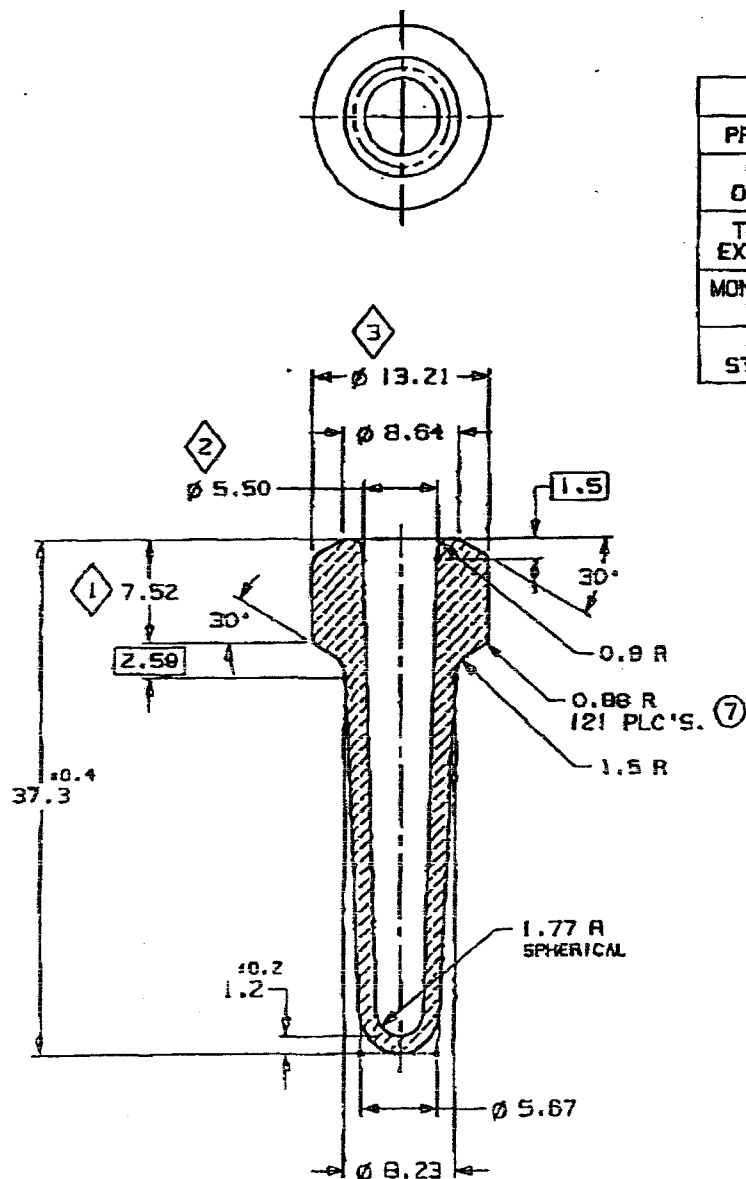
| PHYSICAL PROPERTIES | |
|---|---|
| PROPERTY | VALUE |
| FIRED DENSITY | 5.53 - 5.76 g/cm³ |
| THERMAL EXPANSION | 6.8 - 8.0 x 10⁻⁶ in/in/°C (40 to 1000 °C) |
| MONOCLINIC PHASE | 17.5 - 24.0 PERCENT |
| BURST STRENGTH | 300 lbs. MINIMUM |

ø 13.21
ø 8.64
ø 5.50
1.5
30°
30°
7.52
2.59
0.9 R
0.88 R
121 PLC'S. ⑦
1.5 R
37.3 ±0.4
1.77 R SPHERICAL
1.2 ±0.2
ø 5.67
ø 8.23
③ ② ① ⑤

PRICES:

1) Element with inner and outer electrodes only

$8.54 each

2) Element with out electrodes only

$6.10 each

TEST PROCEDURES PER APPLICABLE
AC ROCHESTER TEST METHODS.

OUTLINE DRAWING

5619267

METRIC

| | 160E02 | A. STIFF |
| | 4:1 | J. RIX |
| | | G. HAKES |
| | 808 5619D00 | B.N.N. |
| | | R.P.J. 02WR7 |

YTTRIA STABILIZED
ZIRCONIA IMS-2521

ELEMENT

A2 | 5619267

| KEY PRODUCT CHARACTERISTICS | |
|---|---|
| ⊖ SAFETY/ COMPLIANCE | ◇ FIT/ FUNCTION |
| TOTAL ON DRAWING | 3 |
| LAST NUMBER USED | 3 |